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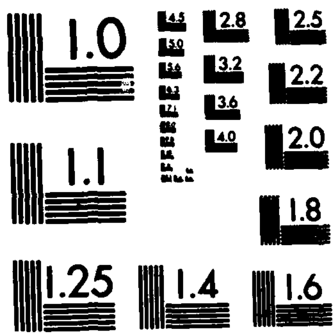

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The subject of this program was a comprehensive study of the preparation and the mechanical, thermal, structural and electrochemical properties of titanium based metallic glasses, with emphasis on their wear properties, as well as an extension of this work to some related transition metal based alloy glasses. This work required several innovations in equipment and experimental techniques as well as construction of specialized facilities, in particular: design of a melt spinner capable of processing reactive alloys, development of a method to measure the Young's modulus of very small samples, and construction of a wear test unit.

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FINAL REPORT

to the

US ARMY RESEARCH OFFICE
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on the program

CHARACTERIZATION OF MECHANICAL, THERMAL AND WEAR PROPERTIES OF TITANIUM RICH METALLIC GLASSES

Proposal	Contract	Program Period
DRXRO-MS-15098	DAAG 29-78-G-0137	1 July 1978 to 30 June 1980
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Submitted by: B.C. Giessen

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Statement of Problem Studied

The subject of this program was a comprehensive study of the preparation and the mechanical, thermal, structural and electrochemical properties of titanium based metallic glasses, with emphasis on their wear properties, as well as an extension of this work to some related transition metal based alloy glasses.

This work required several innovations in equipment and experimental techniques as well as construction of specialized facilities, in particular: design of a melt spinner capable of processing reactive alloys, development of a method to measure the Young's modulus of very small samples, and construction of a wear test unit.

Summary of Principal Results

1. Construction of Arc Furnace Melt Spinner: As mentioned, a principal accomplishment of this program was the construction of a melt spinner capable of processing refractory and/or reactive metal alloys such as those of titanium. This problem was solved by constructing a two-chamber system with an inert gas atmosphere arc furnace in the upper half to melt the alloy, and a melt spinning system in the lower half. This system (which improved upon a design found in the literature) is shown in the appended Fig. 1. It was successfully used to produce ribbons of Ti alloy glasses as well as of other refractory metal alloy glasses. We have reported the details of its design and operation recently at the Third Reston Conference (1). We hope that future improvements of this unit will make it possible to operate it in a continuous mode.
2. Design and Construction of Wear Test Unit: The wear test unit schematically shown in Fig. 2 has been designed and constructed. This unit allows the measurement of the wear and friction coefficients of foil samples produced by rapid quenching. This unit was designed for use with both the short strip pieces obtained by the arc furnace hammer-and-anvil quenching process as well as ribbons obtained by conventional or arc furnace melt spinning. Also, the unit operates both under vacuum and inert gas atmosphere. The unit has been described in a report of work done with it (2).
3. Development of Method for Measuring the Young's Modulus on Short Samples: A major experimental advance of this program has been the adaptation of a method for the measurement of Young's modulus E on short samples to studies of refractory alloy glass samples. Until the development of an arc furnace melt spinner such as the one described above, such samples could only be prepared in the form of short strips (about 1cm long) cut from hammer-and-anvil quenched foils. For these short samples, the standard pulse-echo technique for the dynamic measurement of E is not applicable. Therefore, the impulse-induced esonance (IIR) method of modulus determination was studied and successfully applied; this method had not been previously applied to alloy glasses. In this method, a broad-band pulse is introduced into the sample by an impulse such that the sample selects the resonance frequency which can be monitored by the

transducer. In connection with the known length of the sample, measurement of the frequency allows calculation of the sound velocity which, in turn, yields E if combined with the sample density. This procedure and some results obtained with it have been described in two publications (3, 4).

4. Relationship of Microhardness and Elasticity: We have completed and reported (5) a comprehensive study of the connection between the Young's modulus E and the Vicker's microhardness H_V for many different transition-metal glasses. These glasses belong to three different families (as classified by composition), combining (a) two metals; (b) a transition metal and a metalloid, and (c) two mutually non-substitutional metals (such as Ti and Ni) and a metalloid. This work has included the Ti alloy glasses studied in other phases of this program.

   The principal result of this study was that the data for the metal-metal glasses (a, above) (including non-transition metal alloys) fall on a straight line which can serve as a universal master curve; this relation indicates that the shear strain at the yield point of glassy metals is approximately constant, regardless of their constituents and compositions. The E vs. H_V data for the glasses containing metalloids (b, c) fall on a different, approximately parallel line which is displaced somewhat towards lower values of H_V; this indicates a reduced yield strain for these glassy metals.

5. Wear Tests and Their Results: A principal object of this research program has been the study of sliding wear on Ti alloy glasses as well as on other glasses based on transition metals.

   During the first part of the program, while the wear test unit at Northeastern University was still under construction, wear tests on metallic glasses containing Ti were made at MIT, using the facilities and the professional collaboration of Dr. N. Saka, an associate of Prof. Nam Suh of MIT. Subsequently, we have carried out the bulk of the wear studies using our new unit, incorporating also an extensive microscopic and scanning electron microscopic study of the worn surfaces and the correlation of friction coefficients, wear coefficients and microhardness data as planned. In the following, we describe the wear results in more detail because of their importance.

   Three major families of glassy alloys were tested, with compositions as

shown and with results as summarized in the following Table 1.

Glassy Alloy	Hardness	Wear Coefficient and Wear Rate	Coefficient of Friction	Suggested Mechanism
Ti, Zr base (Early transition metal rich)	Low	Medium	High	Delamination-like and abrasive
Fe, Co, Ni base (Late transition metal rich)	Medium	Low	Low	Adhesive and local fracture
Refractory metal alloy (T_5 - T_9 metals)	High	High	High	Delamination-like and abrasive

The most general observation is that the wear of all metallic glasses studied is characterized by <u>higher</u> wear rates, as compared to crystalline alloys containing these elements. However, comparing the glasses with each other, they can be subdivided based on their relative wear resistance into groups with medium-to-high and lower wear rates:

a) Alloys with medium-to-high wear rates have unique wear surface morphologies and wear debris. The worn surface shows roughness, cracks and grooves; the wear debris consists of small spherical particles, larger aggregates ($\sim 100\mu$) and plate-like, rectangularly shaped debris ($100-200\mu$). These morphological characteristics cannot be distinguished from those resulting from delamination wear of crystalline materials. This high wear rate was observed in Ti- and Zr-rich glasses and refractory metal glasses (typically T_5 - T_9 element glasses such as Ta-Ir).

b) Relatively low wear rates are associated with the low friction region of the friction - wear rate diagram and occur for glassy alloys such as Fe, Ni and Co rich alloys; however, even these glasses show systematically higher wear rates than their counterpart crystalline alloys. Morphologically, localized and fractured round dimples were found on the worn surface of some of these lower-wear-rate alloys; fracture appears to have developed slowly following long adhesive wear.

For the first category, wear behavior cannot be explained by static physical properties such as the Young's and shear moduli since high strength glasses such as T_5 - T_9 metal glasses exhibit the highest wear rates. The wear process is thought to be determined by crack propagation in these alloys and is not due to "simple" adhesive wear, while, for the second category, fundamental physical parameters such as the Young's and shear moduli and the bond character, etc., seem to determine wear behavior.

Alternatively, wear can be analyzed by a direct comparison of hardness and wear rate; the relationship between these two parameters is well established for crystalline systems. While a similar correlation was found in the wear of the present transition metal rich glassy alloys, it is not a universal correlation. Linear correlations exist for each group of alloys in the log-log plot of the hardness and wear rate diagram and these correlations can be described for each alloy group by a single exponent; however, these exponents differ such that there is no universal coefficient for all alloy systems investigated.

The results of the wear resistance work have been described in two publications (2, 6); several additional papers to be based on completed experiments are still in progress (7-9).

6. Compositional Dependence of E, H_v, and T_c of Glassy Alloys: To obtain a comprehensive characterization of the composition dependence of the inter-related (colligative) thermal-elastic-plastic properties for a family of metallic glasses of interest, an extensive study of these properties was carried out on glassy Ti alloys with compositions given by $(Ti_{1-x}Ni_x)_{90}Si_{10}$. Also, the effect of different addition metals M on these properties was studied in glassy alloys with the composition $Ti_{60}M_{30}Si_{10}$ where M = Fe, Co, Ni, Cu. This work has been reported at AIME and MRS meetings and two papers based on this work are in preparation (10, 11).

In the first of these studies (10) a maximum was observed as a function of composition x for E, H_v and T_c. Similar maxima have been seen in other series of glassy binary and ternary alloys; however, the sharpness of the maximum was unexpected and attempts are in progress to model this result in terms of the microscopic structure of metallic glasses.

In the second study (11), i.e., the series of tests on alloys containing different metals M, good correlations of the three properties with each other and the group number (electron concentration) of M were found. This shows that these properties are indeed colligative, i.e. of similar origin, and depend on the electronic structure of the M metal; however, the proper correlation is still under study. Further, a comprehensive study of the elastic properties of Fe, Co, and Ni based amorphous metals was completed in association with H.A. Davies and has been published (12).

7. Theoretical Program: There has been a substantial effort to understand the principles underlying glass formation in order to find simple correlations between fundamental, readily accessible properties and glass formation.

This work has been very successful. Two different approaches have been followed and each has produced a useful two-parameter correlation plot that can be used to predict ready glass formation (RGF) in binary Ti alloys and other alloy systems. In one of these studies (13), RGF was found to be associated with a combination of two phase diagram features such as melting point depression and terminal solid solubility. In the other (14), RGF is correlated with combinations of favorable atomic size ratio and negative heats of formation which can be obtained from standard tabulations.

Some of this work, as well as surveys of correlated thermal and mechanical properties, have also been published in a review (15).

8. Corrosion Tests: In the surface chemical portion of this program, dynamic voltammetric corrosion tests were carried out on Ti-Ni-Si alloy glasses in neutral-to-concentrated acidic chloride solutions. Levels of corrosion resistance comparable to those measured on melt-spun "Metglas" type alloys containing Cr were found. In the series $(Ti_{1-x}Ni_x)_{90}Si_{10}$ the corrosion resistance (as deduced from the height of the passivation plateau) increases with increasing Ni content. This result was initially surprising; we had expected that corrosion resistance would be primarily due to formation of a titanium oxide and would increase with Ti content. We now believe that the corrosion resistance is simply due to the more positive electrochemical potential of the Ni rich alloy and that the Ti richer alloys corrode more because of a

failure to form protective, passivating oxide films on these glasses. Results will be published (16).

9. Comparison of E and H_v of Glasses and Crystalline Alloys: In an extensive study (17), elastic (Young's modulus E) and plastic (microhardness H_v) properties of glassy alloys from two pertinent metallic alloy systems were compared to properties of the corresponding crystalline alloys. Two zirconium alloy systems, Zr-Ni and Zr-Cu, were selected because there are large glass forming composition ranges in both systems and the glassy alloys had also been studied as part of this program (see 6 above). The results were interesting and in part unexpected: (a) While the mechanical properties of the glasses change monotonically, those of the crystalline alloys change discontinuously with composition; (b) While glasses generally have lower moduli than crystalline alloys, one specific alloy phase was found, Zr_2Ni, where the crystalline compound has an abnormally low E value that lies below that of the corresponding glass. The change of H_v with heating is also of interest: H_v generally increases on heating up to a maximum value and then decreases again to the final crystalline value. A paper on these results is in preparation (18).

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1. S.H. Whang and B.C. Giessen, Arc Furnace Melt Spinner for the RSR Processing of Refractory and Reactive Alloys, Proc. Third Restion Conf. on Rapid Solidification Processing, Dec. 1982, in print.

2. S.H. Whang and B.C. Giessen, Wear Properties of Some Ti Alloy Glasses, in Proc. Fourth Internat. Conf. on Rapidly Quenched Metals, Sendai (1981), Vol. 2, T. Masumoto and K. Suzuki, Eds., The Japan Institute of Metals, Sendai, p. 1403.

3. S.H. Whang, L.T. Kabacoff, D.E. Polk and B.C. Giessen, Measurement of Young's Modulus on Small Samples of Amorphous Metals Using the Impulse Induced Resonance Technique, Met. Trans. A, 10A, 1789 (1979).

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9. S.H. Whang and B.C. Giessen, Anomalous Wear Behavior of Refractory Glassy T_5 - T_9 Alloys (Nb, Ta, Ir, Rh), in preparation.

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17. E. Wong, M. Sc. Thesis, Northeastern University, Boston, MA, 1982.

18. E. Wong, S.H. Whang and B.C. Giessen, Comparison of Elastic and Plastic Properties of Glassy and Crystalline Zr-Ni and Zr-Cu Alloys, in preparation.

Summary of Status of Publications

Published: 2, 3, 4, 5, 6, 12, 15, 17 (Thesis);
In Print: 1, 13;
In Preparation (Experimental work completed): 7, 8, 9, 10, 11, 14, 16, 18.

Presentations

1. S.H. Whang, R. Finocchiaro, D.E. Polk and B.C. Giessen, "Mechanical and Thermal Properties of $Ti_{60}TM_{30}Si_{10}$ and other Ti-rich Metallic Glasses", Sept. 17, 1979, TMS-AIME Fall Meeting, Milwaukee, WI.
2. S.H. Whang, L.T. Kabacoff, D.E. Polk and B.C. Giessen, "Measurement of Young's Modulus on Small Samples of Amorphous Metals Using the Impulse Induced Resonance Techniques, Sept. 17, 1979, TMS-AIME Fall Meeting Milwaukee, WI.
3. C.L. Tsai, S.H. Whang and B.C. Giessen, "Corrosion Behavior of Ti-rich Glassy Alloys", Oct. 8, 1980, TMS-AIME Fall Meeting, Pittsburgh, PA.
4. S.H. Whang, C.L. Tsai and B.C. Giessen, "Measurement of Shear Modulus on Ribbon Slope Amorphous Sample with a Rectangular Cross Section", March 25, 1980 American Physical Society Meeting, NY.
5. S.H. Whang, "Mechanical and Thermal Properties of Ti-rich Glasses", April 10, 1980 at Naval Surface Weapon Center, White Oak Lab., Silver Spring, MD.
6. S.H. Whang and B.C. Giessen, "Wear Properties of Ti Containing Glassy Alloys", Oct. 8, 1980, TMS-AIME Fall Meeting, Pittsburg, PA.
7. S.H. Whang, D.E. Polk and B.C. Giessen, "Hardness vs. Young's Modulus of Metallic Glass", Aug. 27, 1981, Fourth International Conference on Rapidly Quenched Metals, Sendai Civic Hall, Sendai, Japan.
8. S.H. Whang and B.C. Giessen, "Strength and Wear Properties of Ti-rich Glassy Alloys", Aug. 27, 1981, Sendai, Japan.
9. S.H. Whang, "Prediction of Ready Glass Formation in Binary Alloy System", Oct. 13, 1981, TMS-AIME Fall Meeting, Louisville, KY.
10. S.H. Whang and B.C. Giessen, "Wear Properties of Some Fe, Co and Ni Base Glassy Alloys", Oct. 15, 1981, Louisville, KY.
11. S.H. Whang and B.C. Giessen, "Wear of Transition Metal Rich Glassy Alloys", Nov. 19, 1981, MRS Meeting, Boston, MA.

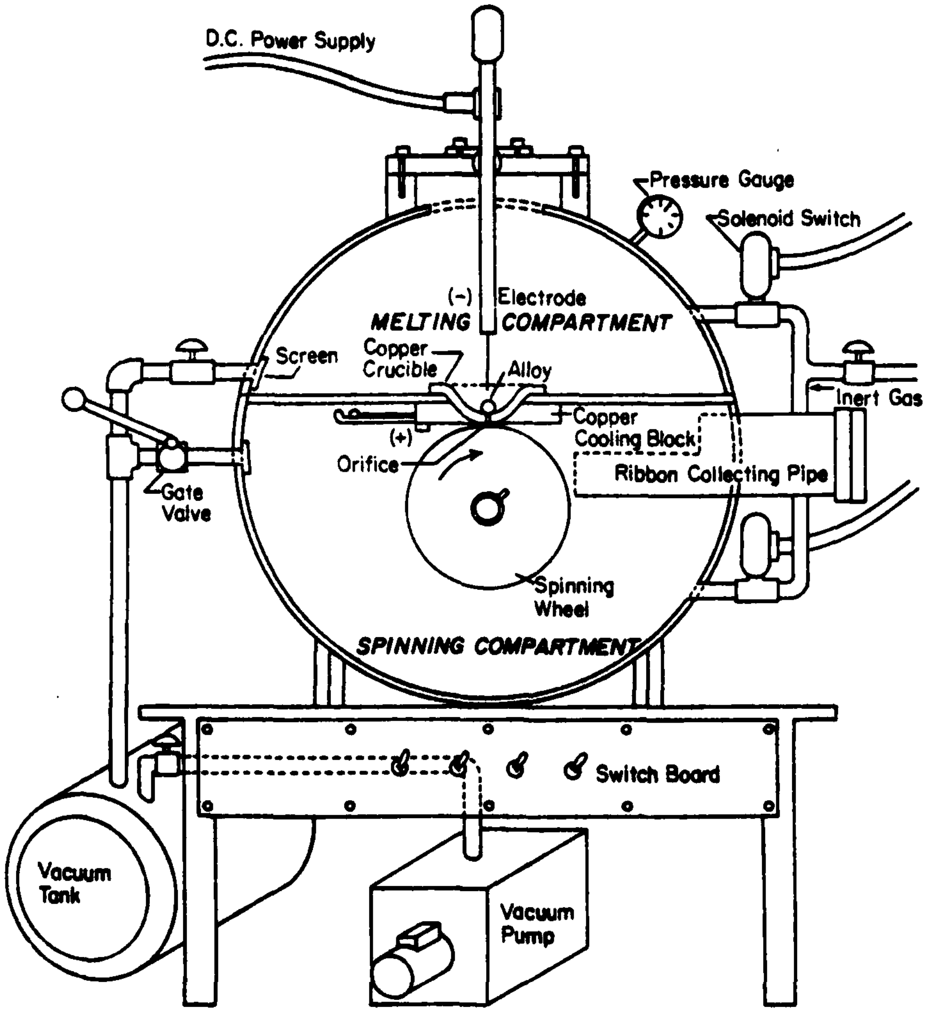

Fig. 1 Schematic diagram of the arc furnace melt spinner constructed at Northeastern University. A motor which drives the spinning wheel is located behind the main chamber.

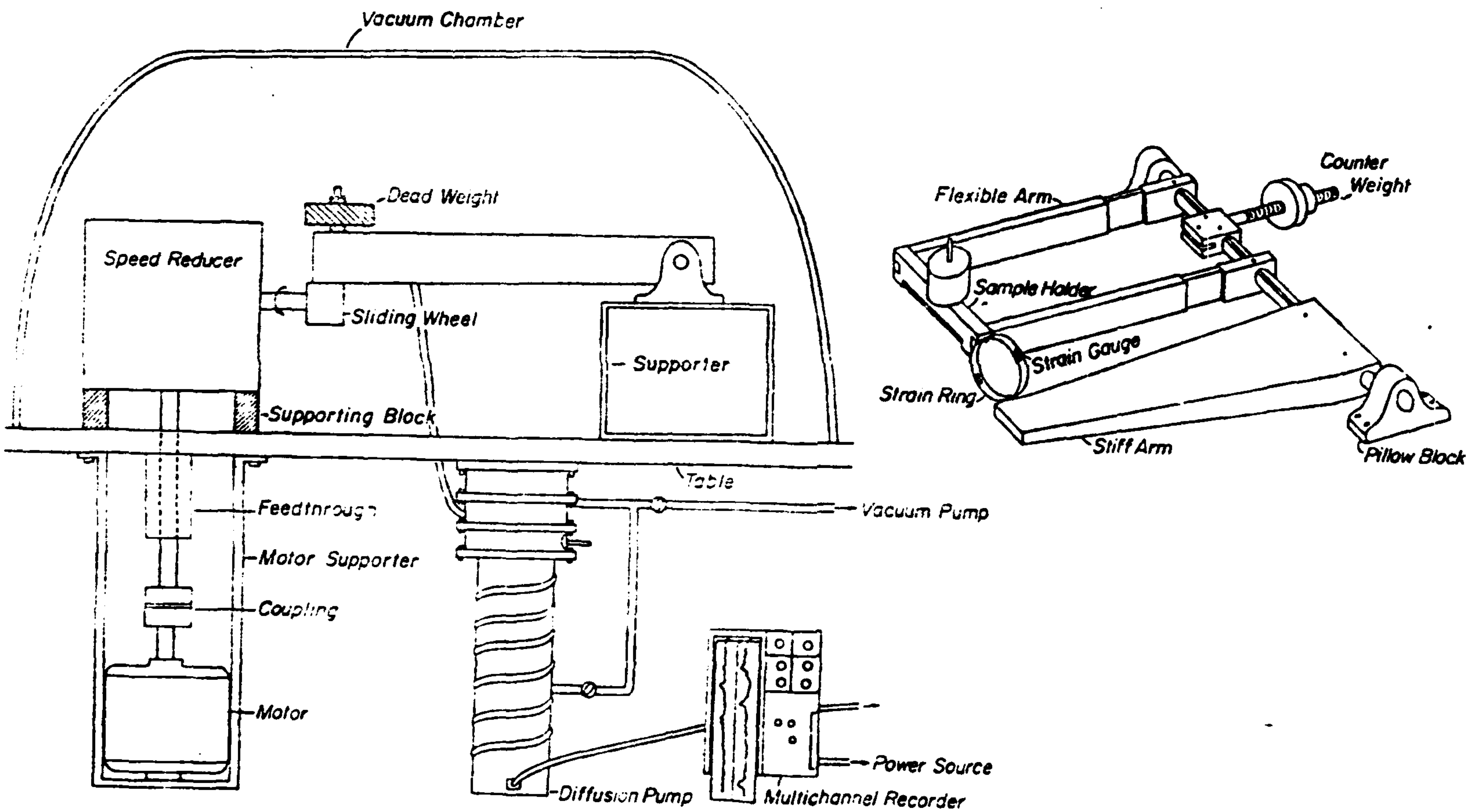

Fig. 2 Wear test unit

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DEGREES GRANTED:

E. Wong, M.Sc., 1982